Inorganica Chimica Acta, 17 (1976) 221–224
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The Reactivity of Complexed Carbocycles. I. Nucleophilic Addition of Lewis Bases to Tropylium and Homotropylium Derivatives of Molybdenum and Tungsten Carbonyls

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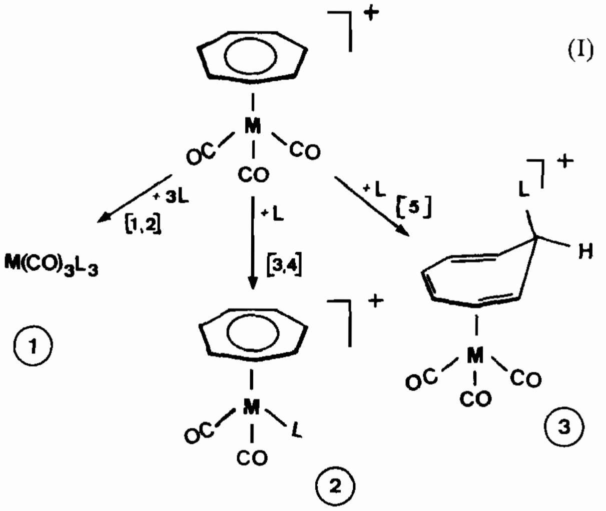
Received August 4, 1975

The reaction of tropylium and homotropylium complexes of molybdenum and tungsten with alkylphosphines has been investigated. Ring addition is observed when low temperatures are maintained, while ring- or CO-substitution occurs at room temperature. A mechanistic scheme for these reactions is proposed. The compounds $[C_7H_7Mo(CO)_2L]^+$ *react with triisopropylphosphine* $[P(ipr)_3]$ *with substitution of L, while* $[C_7H_9W(CO)_3L]^+$ *is attacked by* $P(ipr)_3$ *at the carbocyclic ring, giving a phosphonium salt.*

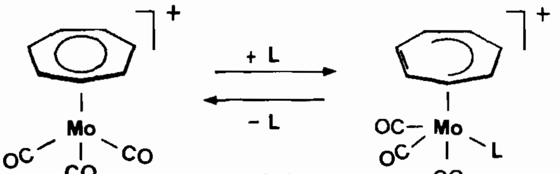
Introduction

The reaction of Lewis bases L, *e.g.* tertiary phosphines, with $[C_7H_7M(CO)_3]^+$ (M = Cr, Mo, W) has received considerable attention in recent times. Three different routes, by which this reaction can proceed, have been established:[1–5]



(I)

The course of the reaction is influenced by either i) the stoichiometric amounts of ligand L used or ii) the base strength of the nucleophile. If for instance $[C_7H_7Mo(CO)_3]^+$ is treated with an excess of triphenylphosphine $[PPh_3]$ the only product is *fac*-$[Mo(CO)_3(PPh_3)_3]$, while use of a 1:1 molar ratio leads to good yields of $[C_7H_7Mo(CO)_2PPh_3]^+$.[3]



(II)

For both reaction paths 1 and 2 a similar mechanism has been proposed with the same primary intermediate $[\eta^5\text{-}C_7H_7Mo(CO)_3L]^+$ [2,3] which then reacts either by displacement of a CO group to give the stable $[C_7H_7Mo(CO)_2L]^+$ or by further reaction with L to $[\eta^3\text{-}C_7H_7Mo(CO)_3L_2]^+$ giving ultimately *fac*-$[Mo(CO)_3L_3]$.

The occurrence of reaction path 3 has so far been observed in one example only, the reaction of $[C_7H_7Cr(CO)_3]^+$ with alkylphosphines.[5] Similar ring additions of tertiary phosphines to $[\pi\text{-}C_4H_4Fe(CO)_2NO]^+$ [6] and to cyclic dienyl iron tricarbonyls[7] have previously been described. The 16-electron compound $[C_7H_9Mo(CO)_3]BF_4$ also adds triphenylphosphine not at the metal (as would be expected) but at the ring, giving the phosphonium salt $[C_7H_9PPh_3]BF_4$ and $Mo(CO)_3(PPh_3)_3$.[8]

The aim of these studies was to show that reaction path 3 is in fact under suitable conditions possible for most compounds $[\pi\text{-trienylM(CO)}_3]^+$ (M = Cr, Mo, W), although two authors[4,5] found that reaction of $[C_7H_7Mo(CO)_3]^+$ with alkylphosphines only leads to ring displacement and formation of $Mo(CO)_3L_3$ as the main product, no ring addition (or CO displacement) being observed.

Results and Discussion

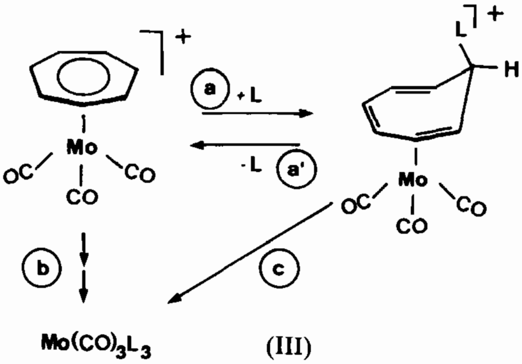
On adding triisopropylphosphine $[P(ipr)_3]$ to a suspension of $[C_7H_7M(CO)_3]BF_4$ (M = Mo, W) in

CH_2Cl_2 at room temperature, an initial colour change of the solution to an intense violet is seen, which however gradually disappears within a minute. The only isolable product after workup is $M(CO)_3L_3$.

On doing the same reaction in a molar ratio of 1 : 1 at –40° C, the violet colour persists and on addition of cold ether violet–red salts precipitate and can be isolated in virtually quantitative yields. On using tri-n-butylphosphine a similar reaction occurs, on addition of ether however only badly manageable oils are obtained.

The violet salts formed from $P(ipr)_3$ and $[C_7H_7M(CO)_3]BF_4$ (M = Mo, W) analyse as $[C_7H_7P(ipr)_3M(CO)_3]BF_4$ and show carbonyl bands (in KBr) at 1880, 1925 and 1980 cm^{-1} for M = Mo and at 1860, 1920 and 2000 for M = W. These absorptions are similar to the neutral compounds $C_7H_8M(CO)_3$ and show that the positive charge is now no longer on the metal. These compounds are better described as phosphonium salts coordinated with a metal tricarbonyl unit.

On dissolving these salts at room temperature in CH_2Cl_2 or $CHCl_3$ the initial violet colour of the solutions disappears after a short time, various products being formed among which $M(CO)_3L_3$. This agrees with the results obtained by Hackett[5] and Graham[4].



(III)

The equilibrium *a*/*a'* for M = Mo, W at room temperature appears to be on the right side, but the fact that solutions of previously isolated $[C_7H_7P(ipr)_3Mo(CO)_3]BF_4$ decompose at room temperature can only be accounted for by some dissociation along route *a'* and further rapid reaction along reaction path *b*. Reaction along route *c* is unlikely under these conditions, as $[C_7H_7Mo(CO)_3]^+$ should be more susceptible to nucleophilic attack at the metal than $[C_7H_7P(ipr)_3Mo(CO)_3]^+$. A further support for this mechanism can be seen in the fact that after workup of the reaction products no phosphonium salts $[C_7H_7P(ipr)_3]^+$ could be isolated which would be formed by reaction along path *c*. A similar equilibrium *a*/*a'* has been observed for the reaction of $[C_7H_7Cr(CO)_3]^+$ with triphenylphosphine at room temperature, where the equilibrium even with large excess of phosphine cannot be completely shifted to the right.[5]

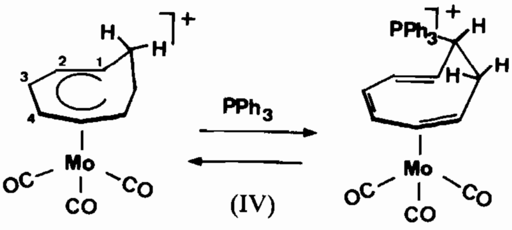
The compounds $[C_7H_7Mo(CO)_2L]^+$ (L = aryl-phosphine, -arsine, -stibine *etc.*)[4] that have recently been described do not react with alkylphosphines by ring addition. Instead, at room temperature $P(ipr)_3$ attacks these compounds at the metal with facile displacement of the weaker nucleophile:

$$[C_7H_7Mo(CO)_2L]^+ + P(ipr)_3 \rightarrow [C_7H_7Mo(CO)_2P(ipr)_3]^+ + L$$

L = PPh_3, $SbPh_3$ *etc.*

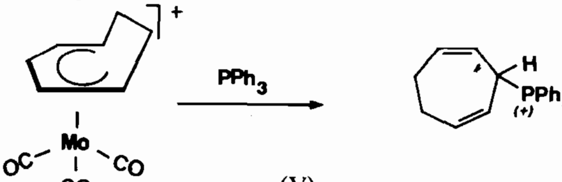
This reaction is quantitative and is a convenient route to compounds $[C_7H_7Mo(CO)_2L]^+$ (L = strong nucleophile), which cannot be made by direct substitution of CO from $[C_7H_7Mo(CO)_3]^+$. This is in fact the first example where, starting initially from $[C_7H_7Mo(CO)_3]^+$, either $Mo(CO)_3L_3$, $[C_7H_7Mo(CO)_2L]^+$ or $[C_7H_7LMo(CO)_3]^+$ can be prepared in good yields for the same ligand L by careful control of the reaction conditions.

On switching to other cationic molybdenum tricarbonyl systems we reacted the homotropylium complex $[C_8H_9Mo(CO)_3]BF_4$[9,10] with PPh_3. A ready reaction occurs in CH_2Cl_2 already at –30° C, the reaction product being again precipitated by addition of cold ether as a yellow powder. The product analyses as $[C_8H_9PPh_3Mo(CO)_3]BF_4$, having CO frequencies of 1900, 1940 and 2000 cm^{-1} (in KBr), indicating again that nucleophilic attack has occurred at the ring system:



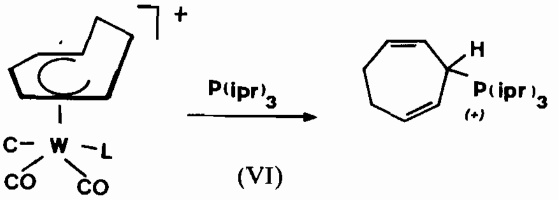
(IV)

The compound is rather unstable in solution (and also in the solid to some extent), no NMR spectrum thus being obtainable. Further experiments are in progress to determine whether PPh_3 (or other nucleophiles such as H^-) attack the ring exclusively in 1-position, giving 1,3,5-cyclooctatriene derivatives or whether some other mode of attack is also possible. It has previously been mentioned that on protonation of $C_7H_8Mo(CO)_3$ with HBF_4 the 16-electron compound $[C_7H_9Mo(CO)_3]BF_4$ is formed, which reacts with PPh_3 with stereospecific nucleophilic addition to the ring:[8]



(V)

Protonation of the corresponding tungsten compound proceeds via the solvated intermediate $[C_7H_9W(CO)_3S]^+$ (S = propionic anhydride) to give on addition of Lewis bases the compounds $[C_7H_9W(CO)_3L]^+$ (L = PPh_3, $AsPh_3$, $SbPh_3$, $P(OMe)_3$ and $P(OPh)_3$).[11] These compounds show no further reaction with PPh_3, they do however react with stronger nucleophiles like $P(ipr)_3$ by attack at the cycloheptadienyl ring and subsequent decomposition to give a phosphonium salt in good yields:



(VI)

On reaction with H^- or MeO^- no definite compounds could be isolated, although a rapid reaction appears to take place.

Taking all quoted results into account, also noting that $[C_7H_7Mo(CO)_3]^+$ reacts with H^- with addition to the ring to $C_7H_8Mo(CO)_3$[12], but with I^- via CO substitution to $C_7H_7Mo(CO)_2I$[13], we come to the conclusion that cationic compounds of the group VI elements (especially Mo and W) with cyclic dienyl- or trienyl systems as ligands tend to react with (i) hard bases (neutral or anionic) at the carbocyclic ring (by addition), (ii) soft bases at the metal (by CO substitution).

Routes (i) and (ii) are kinetically favoured under mild conditions, while by either increasing the concentration of L or raising the temperature the thermodynamically favoured displacement of the carbocyclic ring is observed in most cases.

On introducing a basic ligand L for one CO the direction of the nucleophilic attack can be changed but results appear at the present time somewhat unpredictable, for whereas $[C_7H_7Mo(CO)_2L]^+$ is not attacked by alkylphosphines at the ring (not even at low temperatures) but at the metal, $[C_7H_9W(CO)_3L]^+$ shows a ready reaction with ring addition and formation of a stable phosphonium salt.

Experimental

All experiments were carried out under nitrogen, using solvents that were purified under nitrogen by standard procedures. NMR measurements were made on a JEOL-C-60-HL and IR spectra were obtained on a Beckman IR 12.

$[C_7H_7P(i\text{-}C_3H_7)_3M(CO)_3]BF_4$ (M = Mo, W)

360 mg (for M = Mo) or 450 mg (for M = W) of $[C_7H_7M(CO)_3]BF_4$ (1 mmol) are suspended in 5 ml CH_2Cl_2 and cooled to –40° C. Under stirring 180 mg $P(i\text{-}C_3H_7)_3$ (1.1 mmol) is added. From the resultant clear red solutions violet salts can be precipitated by the addition of 75 ml cold ether. After filtering over a G3 fritted disc the salts are washed with cold ether. Drying affords 500 mg of the molybdenum salt and 600 mg of the tungsten salt. Yield 95%. *Anal.* Found: C, 43.87; H, 5.50; Mo, 18.31. $C_{19}H_{28}BF_4MoO_3P$ calcd.: C, 44.04; H, 5.44; Mo, 18.51%. Found: C, 37.57; H, 4.73; W, 30.14. $C_{19}H_{28}BF_4O_3PW$ calcd.: C, 37.65; H, 4.65; W, 30.33%.

$[C_8H_9P(C_6H_5)_3Mo(CO)_3]BF_4$

Preparation as above from 370 mg $[C_8H_9Mo(CO)_3]BF_4$[10] (1 mmol) and 290 mg $P(C_6H_5)_3$ (1.1 mmol). Yield 510 mg, 96%. *Anal.* Found: C, 55.14; H, 3.96; Mo, 15.03. $C_{29}H_{24}BF_4O_3PMo$ calcd.: C, 54.92; H, 3.81; Mo, 15.12%.

$[C_7H_7Mo(CO)_2P(i\text{-}C_3H_7)_3]PF_6$

740 mg $[C_7H_7Mo(CO)_2SbPh_3]PF_6$[4] (1 mmol) is dissolved in 10 ml CH_2Cl_2 and treated with 0.5 ml $P(i\text{-}C_3H_7)_3$. After stirring for 5 minutes 75 ml ether is added and the precipitate is filtered and washed. This procedure should be repeated twice to insure complete reaction. Yield 480 mg of a pale brown powder, 87%. *Anal.* Found: C, 39.87; H, 4.92; F, 20.37. $C_{18}H_{28}F_6MoO_2P_2$ calcd.: C, 39.43; H, 5.14; F, 20.7%. IR (cm^{-1}) in KBr: 1980 s, 2019 vs. NMR (in nitromethane-d_3, chemical shift in δ, internal standard TMS): 5.95 ppm (d,$J_{P\text{-}H}$ = 3 Hz, 7H); 2.4 ppm (m, 3H); 1.3 ppm (dd, 18 H).

$[C_7H_9P(i\text{-}C_3H_7)_3]BF_4$

800 mg $[C_7H_9W(CO)_3SbPh_3]BF_4$[11] (1 mmol) are dissolved in 10 ml CH_2Cl_2 and treated with 1 ml $P(i\text{-}C_3H_7)_3$. The solution is stirred for 10 minutes. After adding 75 ml ether a pale brown precipitate forms, which is filtered and washed. The phosphonium salt is extracted from this mixture according to ref. 8. Yield 220 mg, 64%. *Anal.* Found: C, 56.49; H, 8.90; F, 22.11. $C_{16}H_{30}BF_4P$ calcd.: C, 56.49; H, 8.88; F, 22.33%.

Acknowledgments

I am grateful to Prof. H. Werner for generous support and to BASF Ludwigshafen for a gift of cyclooctatetraene. Also financial assistance from the Schweizerische Nationalfonds zur Förderung der wissenschaftlichen Forschung is gratefully acknowledged.

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